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(54) Title of the Invention: POLYOLEFIN COMPOSITION

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Specification

1. Title of the Invention

POLYOLEFIN COMPOSITION

2. Patent Claims

(1) (a) A polyolefin composition, [characterized in that it comprises:]
(b) vegetable fibers with fibrillated cellulose as the main component; and
(c) a nucleating agent in an amount of 0.01-5 parts by weight based on a total of 100 parts by weight of said polyolefin and said vegetable fibers.

(2) The polyolefin composition as described in claim 1, characterized in that said vegetable fibers are contained at a ratio of 10-60 wt.% based on a total of said polyolefin and said vegetable fibers.

(3) The polyolefin composition as described in claim 1 or 2, characterized in that said polyolefin comprises a polyolefin-based adhesive resin.

(4) The polyolefin composition as described in claim 3, characterized in that said polyolefin-based adhesive resin is at least one of (a) modified polyolefin obtained through an addition reaction of an unsaturated carboxylic acid or a derivative thereof with a polyolefin; (b) a copolymer of a polyolefin and an unsaturated carboxylic acid or a derivative thereof; and (c) a copolymer of an olefin and a vinyl ester.

(5) The polyolefin composition as described in claim 4, characterized in that the content ratio of the unsaturated carboxylic acid or a derivative thereof in said modified polyolefin is 0.02-2 wt.%.

(6) The polyolefin composition as described in claim 4, characterized in that the content ratio of the unsaturated carboxylic acid or a derivative thereof in said copolymer of a polyolefin and an unsaturated carboxylic acid or a derivative thereof is 1-50 wt.%.

(7) The polyolefin composition as described in claim 4, characterized in that the content ratio of the vinyl ester in said copolymer of an olefin and a vinyl ester is 1-50 wt.%.

3. Detailed Description of the Invention

(Field of Industrial Use)

The present invention relates to a polyolefin composition for molding that comprises vegetable fibers containing fibrillated cellulose as the main component and having a shortened molding cycle.

(Prior Art Technology)

Polyolefins such as polypropylene have excellent mechanical properties and moldability and are widely used for injection-molded products, extrusion-molded products, and the like.

A variety of fillers and additives have been added to increase mechanical strength of such polyolefins. In particular, cellulose fillers such as crushed wood pieces, pulp, wood chips, chaff, and wastepaper have been suggested for adding with the object of improving mechanical strength, moldability, and dimensional stability. For example, Public Patent Disclosure Bulletin No. 60-158236 disclosed a polyolefin resin composition in which vegetable fibers containing fibrillated cellulose as the main component were blended with a polyolefin resin containing chemically modified polyolefin.

Among the aforesaid cellulose fillers, wastepaper or paper clippings are very effective for obtaining comparatively inexpensive polyolefin compositions for molding.

(Problems Addressed by the Invention)

However, a problem associated with blending a cellulose filler with a polyolefin is that the molding cycle during injection molding is extended because the cellulose itself does not demonstrate a crystallization action. Furthermore, moldability, in particular, mold separation ability is degraded and merits of the cellulose fillers as low-cost materials cannot be fully demonstrated.

Methods including the step of increasing the application frequency of parting agents or changing the molding conditions have been used to resolve the problems of cracking during mold separation, but those methods were not necessarily satisfactory. Another drawbacks of those methods was that the molding cycle was further extended.

Accordingly, it is an object of the present invention to provide a polyolefin composition comprising vegetable fibers containing fibrillated cellulose as the main component, this composition having improved mechanical properties and mold separation ability and shortened molding cycle.

(Means to Resolve the Problems)

The inventors have conducted a comprehensive study to attain the aforesaid object. The results obtained demonstrated that the mold separation ability can be improved and molding cycle can be shortened by blending a nucleating agent with a polyolefin composition containing a cellulose filler such as wastepaper. This finding led to the creation of the present invention.

Thus, the present invention provides a polyolefin composition, characterized in that it comprises: (a) a polyolefin; (b) vegetable fibers comprising fibrillated cellulose as the main component; and (c) a nucleating agent in an amount of 0.01-5 parts by weight based on a total of 100 parts by weight of the polyolefin and the vegetable fibers.

Examples of polyolefins that can be used in accordance with the present invention include homopolymers of alpha-olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, and 1-methylpentene; copolymers of ethylene or propylene with other alpha-olefins; or copolymers of two or more alpha-olefins. The preferred among the aforesaid polyolefins are polypropylene, and propylene-based polymers, for example, random or block copolymers of propylene and ethylene and optionally other α-olefins. Further, the polyolefin can be mixed with an elastomer such as ethylene – propylene rubber, ethylene – propylene – diene copolymer, and the like.

Because the polyolefin is by itself non-polar, a polyolefin-based adhesive resin can be added to increase affinity to vegetable fibers comprising hydrophilic cellulose as the main component and to obtain a high-strength composition. Examples of the polyolefin adhesive resins include:(a) modified polyolefin obtained by addition reaction of an unsaturated carboxylic acid or a derivative thereof to a polyolefin; (b) a copolymer of a polyolefin and an unsaturated carboxylic acid or a derivative thereof; and (c) a copolymer of an olefin and a vinyl ester.

The aforesaid polyolefins can be used as the polyolefins forming a skeleton of the modified polyolefin. Furthermore, examples of unsaturated carboxylic acids or derivatives thereof that are used for the modification of the polyolefin include acrylic acid, methacrylic acid, maleic acid, fumaric acid, citraconic acid, itaconic acid, endo-bicyclo[2, 2, 1]-5-heptane-2, 3-dicarboxylic acid, endo-bicyclo[2, 2, 1]-1, 4, 5, 6, 7, 7-hexachloro-5-heptene-2, 3 – dicarboxylic acid, and cis-4-cyclohexene-1, 2-dicarboxylic acid. Examples of unsaturated carboxylic acid derivatives include acid anhydrides and esters such as maleic anhydride, citraconic anhydride, endo-bi-cyclo[2, 2, 1]-1, 4, 5, 6, 7, 7-hexachloro-5-heptene-2, 3-dicarboxylic anhydride, endo-bicyclo[2, 2, 1]-5-heptene-2, 3-dicarboxylic anhydride, cis-4-cyclohexene-1, 2-dicarboxylic anhydride, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, maleic acid esters (monoester, diester), and the like.

The content ratio of the unsaturated carboxylic acid or a derivative thereof in the modified polyolefin is preferably 0.02-2 wt.%, more preferably 0.05-1 wt.% based on the polyolefin skeleton. Various conventional methods can be used to bring about an addition reaction of the unsaturated carboxylic acid or a derivative thereof with the polyolefin. For example, a reaction initiator such as an organic peroxide can be added and premixed with the polyolefin and the unsaturated carboxylic acid or a derivative thereof, followed by melt kneading.

A variety of compounds can be used as the olefin that is copolymerized with the unsaturated resin or derivative thereof, or vinyl esters, but ethylene and propylene are preferred. The aforesaid acrylic acid is preferred as the unsaturated acid that is copolymerized with ethylene or propylene, and an anhydride of this acid is the preferred derivative thereof. The vinyl ester is represented by the general formula CH_2=CHOCOR, where R is an alkyl group. The preferred vinyl esters are vinyl acetate, vinyl propionate, and vinyl butyrate, and the especially preferred is vinyl acetate. Therefore, examples of the preferred copolymers include ethylene – acrylic acid copolymer, ethylene – methyl acrylate copolymer, ethylene – ethyl acrylate copolymer, ethylene – butyl acrylate copolymer, and ethylene – vinyl acetate copolymer.

The copolymer may be a random or block copolymer. The content ratio of the unsaturated carboxylic acid or a derivative thereof or the vinyl ester in the copolymer is preferably 1-50 wt.%, more preferably 3-40 wt.%.

As described hereinabove, in the present specification, the term "polyolefins" includes olefin homopolymers, copolymers of two or more olefins, olefin elastomers, and polyolefin-based adhesive resins and should be generally interpreted as relating to olefin-based polymers. The polyolefin-based adhesive resin is preferably contained at a ratio of 3 to 90 wt.%, more preferably 10 to 30 wt.%, based on the entire polyolefin.

Examples of vegetable fibers comprising fibrillated cellulose as the main component and are used in accordance with the present invention, include products obtained by sufficiently breaking apart wastepaper, paper clippings, and the like and fibrillating. In order to obtain a polyolefin composition with improved mechanical strength and moldability, the content ratio of the vegetable fibers comprising cellulose as the main component should be 10 to 60 wt.% based on the total of the polyolefin and the vegetable fibers. When this content ratio is less than 10 wt.%, the reinforcing effect of the cellulose becomes insufficient in terms of strength, rigidity, and heat resistance, and when the content ratio exceeds 60%, the product becomes brittle, the flowability thereof degrades, and utility becomes poor. It is preferred that the amount of vegetable fiber added to the composition be 15 to 50 wt.%.

Examples of the nucleating agent used in accordance with the present invention with the object of improving mold separation ability and shortening the molding cycle include alkali metal salts, alkaline earth metal salts, aluminum salts, titanium salts, chromium salts of aliphatic monocarboxylic acids (capronic acid, stearic acid, and the like), aliphatic dicarboxylic acids (succinic acid, glutalic acid, adipic acid, sebacic acid, and the like), aromatic monocarboxylic acids (benzoic acid, cinnamic acid, naphthoic acid, and the like), and aromatic dicarboxylic acids (phthalic acid and the like), and also dibenzylidene sorbitol and derivatives thereof. Specific examples include aluminum salt, titanium salt, and chromium salt of p-t-butylbenzoic acid, sodium β-naphthoate, sodium 1,2-cyclohexanedicarboxylate, sodium succinate, sodium glutalate, sodium caproate, aluminum phenylacetate, sodium cinnamate, and also dibenzylidene sorbitol and derivatives thereof. Specific preferred examples include aluminum monohydroxy di-p-t-butylbenzoic acid, dibenzylidene sorbitol, di-p-methyl benzylidene sorbitol, and di-p-ethylbenzylidene sorbitol. Further fine powders or inorganic substances such as silica and talc are also preferred as nucleating agents.

The aforesaid nucleating agents can be used individually or in combination or 2 [two] or more thereof. The amount of the nucleating agent is preferably 0.01 to 5 parts by weight per a total of 100 parts by weight of polyolefin and vegetable fibers. When this amount is less than 0.01 part by weight, the molding cycle is not shortened and the mold parting ability is not improved. On the other hand, when it is more than 5 parts by weight, the mechanical strength of the molded product obtained is decreased. The preferred amount of the nucleating agent added to the composition is 0.1 to 5.0 parts by weight.

An appropriate antioxidant can be added to the polyolefin composition in accordance with the present invention. Oxidation-preventing agents based on hindered phenols and oxidation-preventing agents based on thioesters are examples of antioxidants that can be added to the polyolefin composition in accordance with the present invention.

Examples of oxidation-preventing agents based on hindered phenols include 2, 6-di-t-butyl-4-methylphenol, 1, 1, 3-tri(2-methyl-4-hydroxy-5-t-butylphenyl)butane, tetrakis[methylene-3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate]methane, n-octadecyl-β-(4'-hydroxy-3', 5'-di-t-butylphenyl)propionate, 1, 3, 5-trimethyl-2, 4, 6-tris(3, 5-di-t-butyl-4-hydroxybenzyl)benzene, tris (3, 5-di-t-butyl-4-hydroxybenzyl)isocianurate.

Examples of oxidation-preventing agents based on thioesters include dilauryl-thio-dipropionate, distearyl-thio-dipropionate, laurylstearyl-thio-dipropionate, myristil-thio-dipropionate, tetrakis(methylene-3-dodecyl-thio-propionate)methane, 4,4'-thio-bis(3-methyl-6-t-butylphenol), 4,4'-thio-bis(2-methyl-6-butylphenol), 2,2'-thio-bis(4-methyl-6-t-butylphenol), and the like.

The amount of the antioxidant added to the composition is 0.05 to 5 parts by weight, preferably 0.1 to 2.0 parts by weight based on 100 parts by weight of the polyolefin – vegetable fibers mixture.

A variety of pigments and inorganic fillers can be added to improve the external appearance of the molded product and a flame retardant can be also added.

The composition in accordance with the present invention can be obtained by blending in a heated and molten state by using a blending apparatus such as a single-screw extruder, a twin-screw extruder, a Banbury mixer roll, a Brabender, a kneader, and the like or a mixing apparatus such as a Henschel mixer. For the specific properties of cellulose fibers to be demonstrated to a full extent, it is preferred that a method be used such that the dispersion of the fibers is good and crushing or carbonization of the fibers is prevented.

(Working Examples)

The present invention will be described below in greater detail based on embodiments thereof. The following test methods were used in the working examples:

Molding cycle: the composition is injected into an injection molding machine and a minimum time (sec) elapsing before the deformations cease occurring when a molding is protruded is measured. This time is considered as a molding cycle time.
Tensile strength: JIS K7113-71.
Flexural modulus: JIS K7203-73.
Izod impact strength: JIS K7110.

Working Examples 1 to 8

Nucleating agents shown in Table 1 and 0.1 part by weight of tetrakis[methylene-3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate]methane as an oxidation-preventing agent were added to 100 parts by weight of a mixture comprising 56 wt.% of a propylene-ethylene random copolymer (ethylene content 2%, MFR30) as a polyolefin, 14 wt.% maleic anhydride modification product of propylene – ethylene block copolymer as a modified polyolefin of an adhesive resin (acid added quantity is 0.15 wt.%), and 30 wt.% newspapers cut finely in advance, and the components were broken apart and blended in a heating mixer.

The broken apart and blended mixtures were cooled and ground to obtain granulated products. The granulated products were molded in an injection-molding machine to obtain samples, and physical properties of the samples were measured.

Comparative Examples 1 to 5

Operations were repeated, samples were produced, and physical properties thereof were measured in the same manner as in Working Example 1, except that no nucleating agent was used or a nucleating agent was used in an amount outside the range specified by the present invention. The results obtained are shown in Table 1.

Table 1

	No.	Nucleating agent		Molding cycle (sec)	Physical properties		
		Chemical name	Parts by weight		Tensile strength (kg/cm^2)	Flexural modulus (kg/cm^2)	Izod impact strength (kg-cm/cm)
Working Examples	1	TBBA	0.0.1	53	450	26,700	3.0
	2	"	0.1	50	455	27,200	2.6
	3	"	1.0	45	455	27,400	2.5
	4	"	5.0	44	460	28,000	2.1
	5	DBS	0.01	54	445	26,400	3.1
	6	"	0.1	52	455	26,900	3.1
	7	"	1.0	47	450	27,000	2.5
	8	"	5.0	47	460	27,200	2.0
Comparative Examples	1	TBBA	-	57	450	26,400	3.3
	2	"	0.005	57	450	26,300	3.3
	3	"	6.0	44	455	27,000	1.9
	4	DBS	0.005	56	450	26,400	3.2
	5	"	6.0	45	460	26,900	1.8

(Notes) TBBA: aluminum monohydroxy-di-p-t-butyl benzoate
DBA: (1,3)(2,4)dibenzylidene sorbitol

Working Examples 9 to 15

A total of 1.0 part by weight of aluminum monohydroxy-d-p-butyl benzoate as a nucleating agent and 0.1 part by weight of tetrakis[methylene-3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate]methane as an oxidation-preventing agent were added to 100 parts by weight of a mixture obtained by mixing a propylene homopolymer (MFR20; H-PP) and a propylene-ethylene block copolymer (ethylene content 7.7%, MFR15; B-PP), and ethylene – propylene copolymer rubber (Mooney viscosity ML_{1+8} (127°C) 20; EPR) as polyolefins, a maleic anhydride modification product of propylene – ethylene block copolymer as a modified polyolefin of an adhesive resin (acid added quantity is 0.15 wt.%; CMP), and newspapers cut finely in advance at the ratios shown in Table 2. The samples were prepared and physical properties were measured in the same manner as in Working Example 1. The results are shown in Table 2.

Comparative Examples 6 to 8

Operations were repeated, samples were produced, and physical properties were measured in the same manner as in Working Examples 9 to 15, except that no nucleating agent was used. The results obtained are shown in Table 2.

Table 2

	No.	Composition (wt.%)					Molding cycle (sec)	Physical properties		
		H-PP	B-PP	EPR	CMP	Newspaper paper		Tensile strength (kg/cm^2)	Flexural modulus (kg/cm^2)	Izod impact strength (kg-cm/cm)
Working Examples	9	56	-	-	14	30	42	510	32,200	1.1
	10	-	56	-	14	30	44	490	29,300	3.2
	11	44.8	-	11.2	14	30	45	425	18,900	10.5
	12	-	66.5	-	3.5	30	44	455	29,000	3.0
	13	-	46	-	14	40	42	465	32,800	3.1
	14	-	76	-	14	10	42	360	19,500	5.1
	15	-	36	-	14	50	41	451	40,500	3.3
Comparative Examples	6	70	-	-	-	30	56	395	28,000	1.3
	7	-	70	-	-	30	56	290	27,200	2.6
	8	56	-	-	14	30	58	290	17,500	10.0

(Effect of the Invention)

The polyolefin composition in accordance with the present invention has excellent mechanical properties because the vegetable fibers consisting of fibrillated cellulose as the main component are dispersed to a very good degree in a polyolefin by means of polyolefin-based adhesive resin and the adhesive bonding of the cellulose and polyolefin is improved. For this reason, this polyolefin composition can be very effectively used in injection-molded products with a large wall thickness such as air conditioner unit cases for automobiles. Furthermore, in the polyolefin composition in accordance with the present invention, crystallization is enhanced by the addition of a nucleating agent, molding cycle is shortened, and separation ability is improved. Therefore, this composition is highly suitable as a resin for molding.

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Certificate of Accuracy

This is to certify that the attached document, Invention for Polyolefin Composition with Public Patent Disclosure Bulletin Number S63-33448, originally written in Japanese, is, to the best of our knowledge and belief, a true, accurate and complete translation into English.

Dated: February 24, 2004

Thomas J. Tobin
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Sworn to and signed before
Me this 24th day of
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